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A METHOD FOR SAFETY MANUFACTURING HIGH-CONCENTRATION OZONE

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Konodo ozon wo anzen ni seizo suru hoho

[A METHOD FOR SAFELY MANUFACTURING HIGH-CONCENTRATION OZONE]

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PATENT APPLICATION

September 29, 1971

To Director, Patent Agency, Takehisa Inoue

1. Name of Invention: A method for safely manufacturing high-concentration ozone

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A METHOD FOR SAFELY MANUFACTURING HIGH-CONCENTRATION OZONE

Range of Claim

A method for safely manufacturing high-concentration ozone characterized by the fact that an ozone generator is cooled by means of the latent heat of evaporation or the sensible heat of liquid oxygen, liquid air, or a liquefied mixture of oxygen and nitrogen, while ozone is generated from these raw materials. After ozone has been generated within the temperature and pressure range where ozone-oxygen, ozone-air, or ozone-oxygen-nitrogen mixtures can be present in liquid form, the ozone is absorbed by liquid oxygen, liquid air, or a liquefied mixture of oxygen and nitrogen, and this is removed outside of the system as a stable homogeneous mixed solution of ozone-oxygen, ozone-air, or ozone-oxygen-nitrogen.

Detailed Description of the Invention

This invention pertains to a method for safely manufacturing high-concentration ozone.

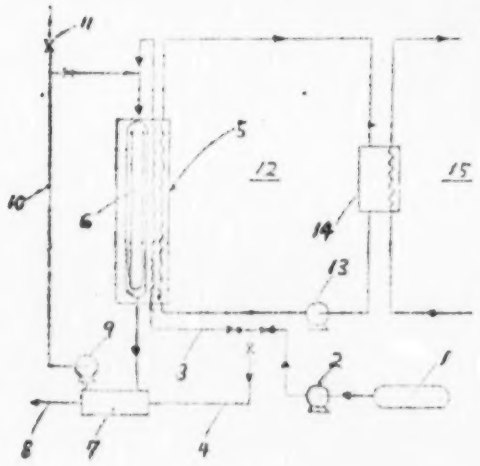
In ordinary ozone generators, most of the electric power is consumed in the form of heat, and the internal temperature will rise. As a result, after ozone has been formed it will once gain be decomposed, and the yield ratio will drop. Consequently, the lower the temperature at which this ozone formation reaction takes place, the better will be the ozone yield ratio. Nevertheless, if the ozone generator is cooled, for example, to a temperature lower than 0° C, this will be extremely costly from the economical point of view on account of the difficulty of adiabatic cooling. Furthermore, if ozone formation is performed below the condensation point of ozone in an attempt to raise the ozone yield ratio as much as possible, there will be safety problems. That is, the ozone will condense inside the ozone generator, producing highly explosive liquid ozone. For this reason, the common practice in the past was to generate ozone while keeping the ozone generator cooled to a temperature in the

vicinity of the normal temperature, and the product obtained was usually only a gas containing a low concentration of ozone on the order of 1 - 3 mol % at most. However, as attention has recently come to be focused suddenly on the pronounced effects of ozone in sterilizing, deodorizing, and bleaching, on the basis of ozone's superior oxidizing power, in connection with the purification of service water and of liquid wastes and with the solution of other pollution problems, there has come to be a demand for ozone with a high concentration. Consequently, it has become necessary to develop a method for manufacturing high-concentration ozone efficiently and safely. The method must be one in which the ozone can be safely processed even when it is condensed.

For this reason, the inventors engaged in a series of various studies aiming at perfecting a method whereby ozone could be generated with a good yield ratio at low temperatures and whereby high-concentration ozone could be safely obtained. As a result, they discovered that it is possible to manufacture ozone with an extremely high concentration of more than 15 mol % at normal pressure with perfect safety and without any danger of explosion, even below the dew point of ozone, by cooling an ozone generator by means of the latent heat of evaporation or the sensible heat of liquid oxygen, liquid air, or a liquefied mixture of oxygen and nitrogen, while generating ozone from these raw materials. The ozone obtained in this manner is immediately dissolved in liquid oxygen, liquid air, or a liquefied mixture of oxygen and nitrogen, and it is continuously removed from the system as a liquid ozone-liquid oxygen, liquid ozone-liquid air, or liquid ozone-liquid oxygen-liquid nitrogen mixed solution. Continuing their studies further, they finally completed this invention.

In the ensuing, this invention is explained in greater detail with reference to a diagram which illustrates one typical mode of application of this invention. In the following description, liquid oxygen is used as the raw material, and a silent discharge tube was used as the ozone generator.

Liquid oxygen stored in a container (or a tank) (1) is pumped into channels (3) and (4) by a pump (2). The liquid oxygen pumped into channel (3) goes into the ozone generator (5). While it cools the electrodes, part or all of it is evaporated, enters the discharge tube (6), and is transformed into ozone.



Next, an ozone-oxygen or ozone-oxygen-nitrogen mixture (gaseous and/or liquid) and/or condensed ozone immediately enters the ozone absorption unit (7), where they are dissolved in the liquid oxygen pumped in from channel (4). The uniform liquid mixture of ozone and oxygen is removed continuously from the removal part (8). In this manner, even if the ozone is condensed in the ozone generator section, it is immediately taken outside the system in the form of a liquid mixture of ozone and oxygen. In this case, there is no danger of explosion whatsoever, since the ozone will form a homogeneous mixed liquid with the liquid oxygen if the ozone concentration is less than 17.6 mol % at normal pressure, or less than 25 mol % at increased pressure. Besides, it is naturally permissible to supply the liquid oxygen for absorbing the ozone directly from a separate channel, rather than from the container (1).

The gaseous oxygen which is generated during the absorption of the ozone in the ozone absorption unit (7) is pumped out by pump (9) through channel (10) and is returned again to the discharge tube (6). In cases when there are excessively large quantities of gaseous oxygen passing through channel (10), it is desirable to introduce part of it into a reliquefaction process (not shown in the diagram) via valve (11).

In cases when the ozone generator (5) cannot be cooled sufficiently merely by the latent heat of evaporation and the sensible heat of the liquid oxygen, it would be desirable to cool by means of primary refrigerants, such as intert gases or liquids like nitrogen, oxygen, argon, or helium circulating through a circulating channel (12). This primary refrigerant would be pumped into the ozone generator (5) by the pump (13); after cooling the discharge tube (6), it would perform heat exchange in (14) with the secondary refrigerant (freons,liquefied methane, liquefied hydrocarbons, etc.) circulating through circulating channel (15), and would be pumped back into the ozone generator (5).

In the application illustrated in the diagram, the liquid oxygen is pumped into the ozone generator (5), where the liquid oxygen is evaporated while it cools the ozone generator. However, as mentioned above, the cooling of the ozone generator can be performed by a refrigerant alone, and the evaporation of the liquid oxygen (as the raw material gas for conversion into ozone) can also be performed by means of heat exchange with a refrigerant in a separately installed heat exchanger.

Needless to say, the temperatures and pressures in the ozone absorption unit (7) and the removal part (8) must be the temperatures and pressures at which the ozone-oxygen mixture can be present in the liquid state.

In the explanation given above, it was assumed that liquid oxygen would be used as the raw material, and that a silent discharge tube would be used as the ozone generator. However, it is possible to use liquid air or a liquefied mixture of oxygen and nitrogen as the raw materials. As the method of generating ozone, it is also possible to combine the discharge method with other methods such as the ultraviolet ray irradiation method, the radioactivity method, or the supersonic wave method.

As mentioned above, this invention makes effective use, in the efficient generation of ozone at low temperatures, of the latent

heat of evaporation and the sensible heat of liquid oxygen, liquid air, or a liquefied mixture of oxygen and nitrogen, which are the raw materials for manufacturing ozone. Furthermore, the ozone which is generated is immediately dissolved in liquid oxygen, liquid air, or a liquefied mixture of oxygen and nitrogen. Thanks to this novel composition which had never been imagined by anyone previously, it will make a remarkable contribution to the safe manufacture of high concentrations of ozone, on which attention has suddenly been focused in recent times in connection with the purification of service water and liquid wastes, and with the solution of other pollution problems.

Example of Application

A concentric double cylinder type discharge tube made of Pyrex glass (discharging gap 4 mm) was used as the ozone generator. The inner tube, which serves as the internal electrode (Ag was deposited by evaporation on its interior) was cooled by the raw material liquid oxygen; the outer tube, which serves as the outer electrode (Ag was deposited by evaporation on its external surface) was cooled by [*] liquid nitrogen.

The power source was 60 c/s, A.C. 100 V. Discharge was produced by using a high voltage transformer to boost the voltage to 10 kV.

The flow rate of the raw material liquid oxygen was 50 ml/hr. It was pumped into the ozone generator (5) at a rate of 18.5 ml/hr, and into the ozone absorption unit (7) at a rate of 31.5 ml/hr. At the same time, liquid nitrogen was supplied at a flow rate of 130 ml/nr to cool the outer electrode. Discharge was performed while maintaining the gas temperature at the discharge tube outlet at - 150° C, and ozone was obtained at a rate of 8 g/hr. Most of the ozone which was formed (about 90%) was condensed in the discharge section and flowed down immediately into the ozone absorption unit (7), where it was absorbed into the liquid oxygen which was pumped

*Translator's note: Illegible in the original foreign text.

in at a rate of 31.5 ml/hr, as mentioned above. About 10% of the ozone formed in the discharge section was not condensed; it assumed the form of a mixed gas of ozone and oxygen of approximately 2 mol %; this also was absorbed in the ozone absorption unit (7). In this manner, a homogeneous mixed solution of 10 mol % of lizuid ozone and liquid oxygen was removed outside of the system from the removal part (8) at a rate of 47.6 mlg/hr. The oxygen gas (3.7 g/hr) formed in the ozone absorption unit (7) during absorption of ozone was recirculated in the ozone generator (5). In this example of application, there was an extremely superior ozone yield ratio of 588 g/kWh, and an energy efficiency of 51%.

Brief Explanation of the Diagram

The diagram is the flow sheet of an example of an actual application of this invention. The power source and the transformer required for discharge are not shown in the diagram.

1 — container for liquid oxygen, liquid air, or liquefied mixture of oxygen and nitrogen; 2 — pump; 3, 4 — channels for liquid oxygen, etc.; 5 — ozone generator; 6 — discharge tube; 7 — ozone absorption unit; 8 — removal part; 9 — pump; 10 — channel; 11 — valve; 12 — circulating channel of primary refrigerant; 13 — pump; 14 — heat exchanger; 15 — circulating channel of secondary refrigerant.